1748 *Inorg. Chem.* **1981**, *20*, 1748-1751

Contribution from the Department of Chemistry,
University of Rajasthan, Jaipur 302004, India

# Kinetics and Mechanism of the Iron(III)-Catalyzed Oxidation of Hydrazine with Peroxydisulfate in Acid Medium

S. S. GUPTA and Y. K. GUPTA*

*Received March 28, 1980*

The oxidation of hydrazine with peroxydisulfate studied in acetate buffer is catalyzed by iron(III). The catalysis operated through the formation of mixed-ligand complexes of Fe(III), $FeS_2O_8{\cdot}N_2H_4^+$ ($K_1$, $k_1$), $FeS_2O_8{\cdot}N_2H_4{\cdot}N_2H_5^{5+}$ ($K_2$), and $FeS_2O_8(N_2H_4)_2^+$ ($K_3$, $k_2$), of which the first and the third are kinetically reactive. The formation constants of the three complexes $K_1$, $K_2$, and $K_3$ and rate constants $k_1$ and $k_2$ were found to be 8.9 ± 2.9, 176 ± 36 $M^{-1}$, and (2.25 ± 0.1) × $10^{-3}$ M and (2.0 ± 0.2) × $10^{-3}$ $s^{-1}$ and (4.9 ± 0.5) × $10^{-3}$ $s^{-1}$, respectively, at 45 °C and $I = 0.1$ M. The formation constants are almost independent of temperature. There was no evidence for complex formation between $Fe^{3+}$ and $N_2H_4$ from kinetics or spectrophotometric results. There is marginal spectrophotometric evidence for a complex of $Fe^{3+}$ and $S_2O_8^{2-}$.

The uncatalyzed oxidation of hydrazine with peroxydisulfate is very slow and has not been investigated, but silver(I)-[1] and copper(II)-catalyzed[2] oxidations have been studied. Silver(I) catalysis operates through the well-known Ag(I)/Ag(II), Ag(III) cycle. With regard to copper(II), there is sufficient evidence for complex formation between copper(II) and hydrazine and between copper(II) and peroxydisulfate, but no positive evidence for the Cu(II)/Cu(III) or Cu(II)/Cu(I) cycle. For the operation of any of these two cycles, it is known that the formation[3] of copper(III) is facilitated in the alkaline solutions and copper(I) disproportionates[4] in acid medium unless it is stabilized by complex formation[5] with a suitable ligand. Iron(II) and iron(III) both are fairly stable in acid medium and have sufficient complexing tendency, and hence catalysis by iron(II) or iron(III) may be considered. Kolthoff and co-workers[6] have used a mixture of iron(II) and peroxydisulfate for the induced oxidation of arsenic(III) and studied the kinetics of the iron(II)-catalyzed oxidation[7] of arsenic(III) with peroxydisulfate. The mechanism is complicated, involving free radicals and arsenic(IV) as an intermediate. A systematic study of the iron(II) catalysis in peroxydisulfate oxidations does not seem to have been made. Hydrazine was considered to be a suitable choice to begin such a study since it is likely to form complexes with either iron(II) or iron(III).

## Experimental Section

**Materials.** Potassium peroxydisulfate, hydrazinium sulfate, hydrazinium hydrate, iron(II) sulfate, sodium acetate, and acetic acid were BDH AnalaR quality. All other chemicals used in the investigation were E. Merck G.R. grade. Solutions were prepared in doubly distilled water (second distillation being from permanganate). All glass vessels were either Pyrex or Corning.

A preliminary study indicated that even the catalyzed reaction is very slow below a pH of 1. A convenient pH for conventional study was found to be 2. Since there is an increase of hydrogen ion concentration during the course of reaction, the pH would not remain constant, and hence an acetate buffer containing 0.016 M sodium acetate and 0.0448 M acetic acid was employed to yield the desired pH. The latter was determined only after the addition of hydrazinium sulfate. In the variation of the concentration of hydrazine from 6.0 × $10^{-4}$ to 6 × $10^{-2}$ M, the pH of the system changed even in the buffer solution. The desired pH was kept constant by the additions of small amounts of solutions of perchloric acid or caustic soda.

**Kinetic Procedure.** Calculated quantities of iron(II) sulfate, sodium acetate, acetic acid, and hydrazinium sulfate were put in the reaction vessel placed in a thermostatic water bath at 45 ± 0.1°. The reaction was initiated by adding temperature equilibrated peroxydisulfate solution. Periodically 5-mL aliquots were analyzed for peroxydisulfate iodometrically. The iodometric method is a combination and modification of the methods of Frigerio[8] and Szabo and his co-workers.[9] The reaction mixture was added to a titration flask containing a known concentration of Cu(II), dilute $H_2SO_4$, and about 1 g of KI. The liberated iodine was titrated against a standard solution of thiosulfate. High concentration of KI and the presence of Cu(II) and Fe(III) resulted in quantitative liberation of iodine from KI by peroxydisulfate. The presence of ~0.1 M $H_2SO_4$ in the titration flask prevented iodine from reacting with the hydrazine present in the aliquots. A blank for Cu(II), Fe(III), and $H_2SO_4$ of the concentrations employed was also determined. In the variation of hydrazine, specially for its lower concentrations, the kinetics were followed by estimating hydrazine by titration[10] against a standard solution of potassium bromate with the use of indigo as indicator.

Since the rate has complex dependence on the concentration of hydrazine, the data were treated for the initial rates by the plane mirror method.[11] Duplicate rate measurements were reproducible to ±5%.

The study of a few preliminary reactions indicated that the reaction mixtures flushed with nitrogen of air yielded results almost identical with those with unflushed mixtures. Nevertheless, the mixtures were flushed with nitrogen before starting the reaction.

Spectrophotometric work was done on a Toshniwal UV spectrophotometer with a 1-cm cell to measure the complex formation between iron(III) and hydrazine or peroxydisulfate in the presence and absence of acetate buffer. The oxidation[12,13] of iron(II) with peroxydisulfate is fast, and hence iron(II) would essentially be present as iron(III). There was no evidence for complex formation between iron(III) and hydrazine, but a complex with hydrazine seems to be formed only in the presence of peroxydisulfate. The absorption of $Fe^{3+}$ in acetate buffer, with and without $S_2O_8^{2-}$, is shown in Figure 1. There is marginal evidence for a complex of $Fe^{3+}$ and $S_2O_8^{2-}$.

## Results

**Stoichiometry.** Reaction mixtures with different concentrations of peroxydisulfate and hydrazine were kept for about 36 h, excess peroxydisulfate was determined iodometrically,[9] and the excess hydrazine was determined by potassium bro-

---

(1) A. O. Dekker, H. A. Levy, and D. M. Yost, *J. Am. Chem. Soc.*, **59**, 2129 (1937).

(2) A. P. Bhargava, Ratan Swaroop, and Y. K. Gupta, *J. Chem. Soc. A*, 2183 (1970).

(3) M. C. Sneed, J. L. Maynard, and R. C. Brasted, "Comprehensive Inorganic Chemistry", Vol. II, D. Van Nostrand, New York, 1954, pp 111-113.

(4) F. Fenwick, *J. Am. Chem. Soc.*, **48**, 860 (1926); H. Heinerth, *Z. Elektrochem.*, **37**, 61 (1931).

(5) D. Senise and E. F. A. Neves, *J. Inorg. Nucl. Chem.*, **34**, 1923 (1972); V. F. Toropova, I. A. Sirotina and T. L. Lisova, *Uch. Zap., Kazan. Gos. Univ.*, **115**, *No. 3*, 43 (1955); C. Kappenstein and R. Hugel, *J. Inorg. Nucl. Chem.*, **36**, 1821 (1974); R. M. Izatt, H. D. Johnston, G. D. Watt, and J. J. Christensen, *Inorg. Chem.*, **6**, 132 (1967).

(6) R. Woods, I. M. Kolthoff, and E. J. Meehan, *J. Am. Chem. Soc.*, **85**, 2385 (1963).

(7) R. Woods, I. M. Kolthoff, and E. J. Meehan, *Inorg. Chem.*, **4**, 697 (1965).

(8) N. A. Frigerio, *Anal. Chem.*, **35**, 412 (1963).

(9) Z. G. Szabo, L. Csanyi, and H. Galiba, *Fresenius' Z. Anal. Chem.*, **132**, 269 (1952).

(10) I. M. Kolthoff, *J. Am. Chem. Soc.*, **46**, 2011 (1924).

(11) M. Latshaw, *J. Am. Chem. Soc.*, **47**, 793 (1925).

(12) I. M. Kolthoff, A. I. Medalia, and H. P. Raaen, *J. Am. Chem. Soc.*, **73**, 1733 (1951).

(13) J. W. L. Fordham and H. L. Williams, *J. Am. Chem. Soc.*, **73**, 4855 (1951).

0020-1669/81/1320-1748$01.25/0

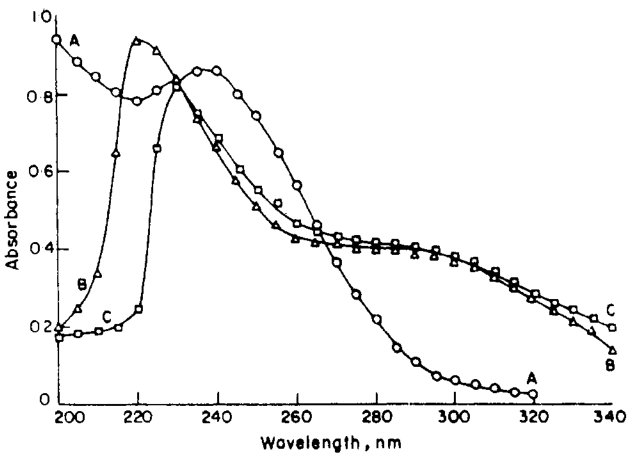


**Figure 1.** Ultraviolet spectrum: A, 2 × $10^{-4}$ M $Fe^{III}$; B, 2 × $10^{-4}$ M $Fe^{III}$ + sodium acetate–acetic acid buffer of pH 2; C, 2 × $10^{-4}$ M $Fe^{III}$ + sodium acetate–acetic acid buffer at pH 2 + 0.01 M $S_2O_8{}^{2-}$.

mate.[10] The stoichiometry was found to be 1:1 under all conditions except when $[N_2H_5{}^+]_0/[S_2O_8{}^2]_0$ was larger than 10. The amount of peroxydisulfate consumed per mole of hydrazine decreases with the increase of this ratio above 10. Hence kinetic studies were made under this limitation. The products were found to be nitrogen, ammonia, and oxygen as found earlier in the Cu(II)-catalyzed study,[2] and this coupled with the results of Bray and Cuy[14] yields the following stoichiometry.

$$4N_2H_5{}^+ + 4S_2O_8{}^{2-} + 2H_2O \rightleftharpoons 2N_2 + 4NH_4{}^+ + 8HSO_4{}^- + O_2 \quad (1)$$

**Fe(II) and Fe(III) Dependence.** The concentration of iron(II) was varied from 6.0 × $10^{-5}$ to 6.0 × $10^{-3}$ M. The plots of $[S_2O_8{}^{2-}]$ and time were straight lines. A plot of rate vs. [Fe(II)] is a straight line passing through the origin. The rates, employing Fe(III) instead of Fe(II), were the same as in case of Fe(II). The observed rate constant, obtained from the slope of the straight line, is 9.4 × $10^{-4}$ $s^{-1}$ at pH 2.0 and 45 °C for $[S_2O_8{}^{2-}] = 10^{-2}$ M and $[N_2H_5{}^+] = 6.0 \times 10^{-2}$ M.

**Peroxydisulfate Dependence.** The concentration of peroxydisulfate was varied from 2.2 × $10^{-3}$ to 4.0 × $10^{-2}$ M at different pH's. The results are shown in Table I. The observed rate constant at pH 2.0 and 45 °C was found to be (90 ± 0.35) × $10^{-4}$ $s^{-1}$, which is similar to one obtained from Fe(II) dependence, though the concentrations of hydrazine in the two cases are different. This, however, is immaterial since the rate is independent of the larger concentrations of hydrazine. The rate constants at pH 2.2 and 2.34 were found to be (13 ± 0.5) × $10^{-4}$ and (51 ± 2) × $10^{-4}$ $s^{-1}$, respectively.

**Hydrazine Dependence.** The concentration of hydrazine sulfate was varied from $10^{-3}$ to 6.0 × $10^{-2}$ M at different [Fe(II)], pH, and temperature. Typical plots of rate vs. $[N_2H_5{}^+]$ are given in Figure 2. The rate increases, attains a maximum, and then decreases to a limiting value with the increase of concentration of hydrazine. The limiting rates for different [Fe(II)], pH, and temperatures are proportional to [Fe(II)], suggesting a particular complex of Fe(III) and hydrazine being present predominantly in the system for the limiting hydrazine concentrations. A limiting rate of 9.8 × $10^{-4}$ $s^{-1}$ at pH 2 is once again similar to the values obtained in other systems. If the rising curves before attaining the maximum are extrapolated to limiting rates, the latter may approximately be taken to correspond to one type of complex. These limiting rates (precision ±15%) at pH 2 and 45 °C are 1.9 × $10^{-6}$, 2.3 × $10^{-6}$, 3.2 × $10^{-6}$, and 9.1 × $10^{-6}$ M $s^{-1}$ for [Fe(II)] = 0.0008, 0.0012, 0.0012, and 0.005 M, respectively. The limiting rates at the same pH and 50 °C and 55 °C are 3.9 × $10^{-6}$ and 4.7 × $10^{-6}$ M $s^{-1}$, respectively, for [Fe(II)] = 0.0016 M. A plot of $(\text{rate})^{-1}$ vs. $[N_2H_5{}^+]^{-1}$ approaches a straight line with a nonzero intercept.

Table I. Variation of Peroxydisulfate in the Fe(II)-Catalyzed Reaction between $S_2O_8{}^{2-}$ and $N_2H_5{}^+$ ([Fe(II)] = 4.0 × $10^{-4}$ M; 45 °C; $I$ = 0.1 M)

| $10^2 \times [S_2O_8{}^{2-}]$, M | $10^2 \times [N_2H_5{}^+]$, M | pH | $10^7 \times$ (rate), M $s^{-1}$ |
|---|---|---|---|
| 0.50 | 4.0 | 2.00 | 3.5 |
| 0.80 | 4.0 | 2.00 | 3.5 |
| 1.00 | 4.0 | 2.00 | 3.4 |
| 2.00 | 4.0 | 2.00 | 3.7 |
| 3.00 | 4.0 | 2.00 | 3.7 |
| 1.00 | 2.0 | 2.20 | 5.0 |
| 1.40 | 2.0 | 2.20 | 5.3 |
| 2.52 | 2.0 | 2.20 | 5.5 |
| 2.92 | 2.0 | 2.20 | 5.7 |
| 3.32 | 2.0 | 2.20 | 5.3 |
| 0.40 | 2.0 | 2.34 | 20 |
| 0.80 | 2.0 | 2.34 | 21 |
| 1.40 | 2.0 | 2.34 | 19 |
| 1.80 | 2.0 | 2.34 | 22 |
| 2.20 | 2.0 | 2.34 | 19 |
| 2.60 | 2.0 | 2.34 | 19 |
| 3.00 | 2.0 | 2.34 | 20 |
| 4.00 | 2.0 | 2.34 | 22 |

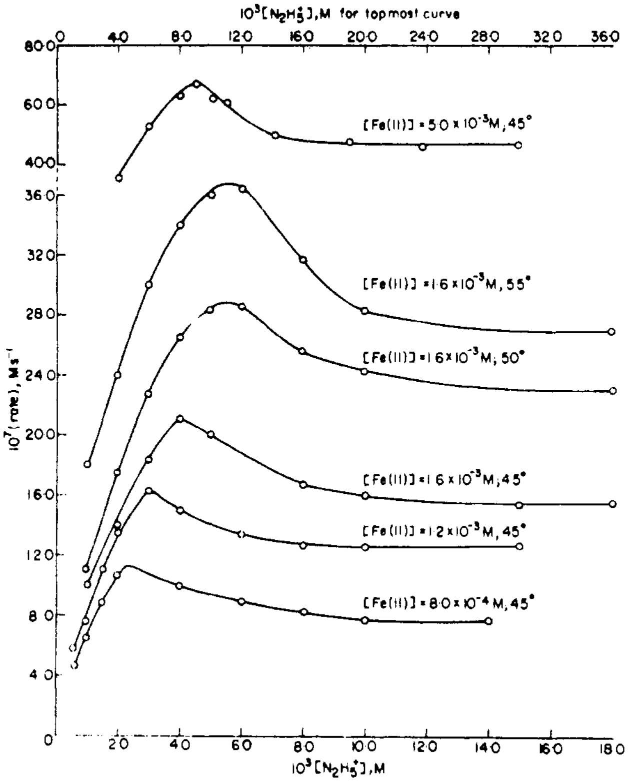


**Figure 2.** Variation of the rate of the $N_2H_4$–$S_2O_8{}^{2-}$ reaction, as catalyzed by Fe(III), with $N_2H_5{}^+$.

A few reactions for hydrazine variation were carried out in 0.01 M $HClO_4$ but without the acetate buffer. Curves characteristic of Figure 2 were obtained, but $[H^+]$ also varied during the course of reaction. Larger $[H^+]$, could not be employed since the reaction was too slow in such systems.

**Hydrogen Ion Dependence.** In view of the complex hydrazine dependence, hydrogen ion effect was studied for two concentration ranges of hydrazine: (1) at less than those

---

(14) W. C. Bray and E. J. Cuy, *J. Am. Chem. Soc.*, **46**, 1810 (1924).

**Table II.** Hydrogen Ion Dependence in the Range of $[N_2H_5^+]$ Less Than That Corresponding to the Maximum Rate ($[Fe(II)] = 1.60 \times 10^{-3}$ M; $[S_2O_8^{2-}] = 10^{-2}$ M; $I = 0.1$ M)

| | | | | | |
|---|---|---|---|---|---|
| $[N_2H_5^+] = 2.0 \times 10^{-3}$ M (45 °C) | | | | | |
| $10^3[H^+]$, M | 1.95 | 7.94 | 17.0 | 25.7 | 36.3 |
| $10^6$(rate), M $s^{-1}$ | 2.1 | 1.4 | 0.90 | 0.78 | 0.66 |
| $[N_2H_5^+] = 2.5 \times 10^{-3}$ M (45 °C) | | | | | |
| $10^3[H^+]$, M | 3.47 | 10.0 | 17.8 | 26.9 | 35.5 |
| $10^6$(rate), M $s^{-1}$ | 2.0 | 1.4 | 1.1 | 0.83 | 0.75 |
| $[N_2H_5^+] = 3.0 \times 10^{-3}$ M (45 °C) | | | | | |
| $10^3[H^+]$, M | 2.34 | 9.55 | 17.0 | 26.9 | 35.5 |
| $10^6$(rate), M $s^{-1}$ | 1.8 | 1.5 | 1.2 | 0.90 | 0.78 |
| $[N_2H_5^+] = 3.0 \times 10^{-3}$ M (50 °C) | | | | | |
| $10^3[H^+]$, M | 2.34 | 9.55 | 17.0 | 26.9 | 35.5 |
| $10^6$(rate), M $s^{-1}$ | 3.7 | 2.2 | 1.7 | 1.4 | 1.3 |
| $[N_2H_5^+] = 3.0 \times 10^{-3}$ M (55 °C) | | | | | |
| $10^3[H^+]$, M | 2.34 | 9.55 | 17.0 | 26.9 | 35.5 |
| $10^6$(rate), M $s^{-1}$ | 5.2 | 3.5 | 2.3 | 2.6 | 1.7 |

**Table III.** Hydrogen Ion Dependence in the Limiting Range of Hydrazine Concentration ($[S_2O_8^{2-}] = 1.0 \times 10^{-2}$ M; $[N_2H_5^+] = 4.0 \times 10^{-2}$ M; $[Fe(II)] = 4.0 \times 10^{-4}$ M; $I = 0.1$ M)

| | $10^6$(rate), M $s^{-1}$ | | |
|---|---|---|---|
| $10^2[H^+]$, M | 45 °C | 50 °C | 55 °C |
| 1.26 | 0.25 | 0.51 | 0.96 |
| 1.175 | 0.28 | 0.55 | 1.1 |
| 1.07 | 0.32 | 0.62 | 1.3 |
| 0.912 | 0.38 | 0.71 | 1.4 |
| 0.631 | 0.47 | 0.94 | 2.0 |
| 0.363 | 0.75 | 1.25 | 2.8 |
| 0.240 | 0.88 | 1.6 | 3.9 |
| 0.135 | 1.16 | 2.2 | 5.0 |

**Table IV.** Effect of Ionic Strength in the Fe(II)-Catalyzed Oxidation of $N_2H_5^+$ with $S_2O_8^{2-}$ ($[S_2O_8^{2-}] = 10^{-2}$ M; $[N_2H_5^+] = 4.0 \times 10^{-2}$ M; $[Fe(II)] = 4.0 \times 10^{-4}$ M; pH 2.0; 45 °C)

| | | | | | | |
|---|---|---|---|---|---|---|
| $[LiClO_4]$, M | 0.05 | 0.1 | 0.2 | 0.5 | 0.75 | 1.0 |
| $10^7$(rate), M $s^{-1}$ | 3.6 | 3.5 | 3.6 | 3.5 | 3.6 | 3.5 |

concentrations corresponding to the maximum when only one complex is likely to be present predominantly and (2) at larger concentrations of hydrazine when limiting rate is obtained. The rate decreases with the increase of hydrogen ion concentration. These results at different hydrazine concentrations and different temperatures are shown in Tables II and III. If a plot of $(\text{rate})^{-1}$ vs. $[H^+]$ is made for a concentration of $N_2H_5^+$ less than that corresponding to the maximum of Figure 2, a straight line with a nonzero intercept is obtained. A similar plot for limiting hydrazine also yields a straight line with a positive intercept.

**Effect of Acetate.** The concentration of sodium acetate was varied along with the concentration of acetic acid in such a way that the concentration of acetate changed without or with only slight change in pH. There is no change in the rate with the variation in acetate ion concentration.

**Effect of Ionic Strength.** The ionic strength was varied (0.05–1.0 M) with lithium perchlorate with fixed concentrations of peroxydisulfate, hydrazine, and iron(II) at pH 2. There was no change in the rate as is obvious from Table IV.

## Discussion

A complex of Fe(III) and peroxydisulfate has not been reported so far, nor is there kinetic evidence in the present system, though there is some evidence from spectrophotometric work. Kinetic evidence for a complex formation has been obtained in the iron(II)-catalyzed oxidation[15] of hydroxylamine with peroxydisulfate. Moreover its complexes with copper(II)[2,16] and silver(I)[17] have also been reported. A complex or ion pair with peroxydisulfate has been indicated in the oxidation of Fe(II) complexes of 1,10-phenanthroline or 2,2′-bipyridyl with peroxydisulfate.[18] Thus under the conditions of the investigation, iron(III) seems to be present almost wholly in the form of peroxydisulfate complex.

The system further becomes complicated by the presence of two other potential ligands, hydrazine and acetate. From other studies[19,20] there is no kinetic or spectrophotometric evidence for a complex between Fe(III) and hydrazine—not even in the presence of acetate ions. Acetate ions and acetic acid seem to play only the role of buffering action. Whether any of their complexes are involved is not indicated by the kinetic results. It appears that the hydrazine cannot form a stable complex with iron(III) alone but can do so with a complex of peroxydisulfate, forming a ternary complex which is more stable.[21] The situation[22] is somewhat similar to the facile formation of a ternary complex between copper(II) $Cu^{2+}$(2,2′-bpy) + 2,2′-bipyridyl and $H_2O_2$ rather than the binary complex between $Cu^{2+}$ copper(II) aquo and $H_2O_2$. Fe(III) is substitution labile and introduction of 1 mol of hydrazine into the complex does not hinder the substitution[23] by another molecule of hydrazine. Thus ternary and quaternary complexes of iron(III) consisting of $S_2O_8^{2-}$ and $N_2H_4$ may be formed.

The following observations should be recognized before any mechanism may be suggested.

(1) Fe(II) is present as Fe(III) and the order is 1.

(2) Fe(III) is present predominantly as a peroxydisulfate complex, perhaps as $FeS_2O_8^+$.

(3) The rate is independent of peroxydisulfate.

(4) The reaction has inverse hydrogen ion dependence, but the order is less than 1.

(5) So far as hydrazine dependence is concerned, the rate law has two limiting forms: one before the maximum in the rate is obtained and the other is for the limiting rate at large $[N_2H_5^+]$. This suggests the involvement of two types of hydrazine complexes. However, inverse hydrogen ion dependence of the limiting rate at large $[N_2H_5^+]$ shows that a third complex is also involved. Thus, there may be three complexes and two of them may be kinetically active.

(6) The limiting rate laws for the two situations are given by (2) and (3) where $A$, $B$, and $C$ are constants.

$$\text{rate} = -d[S_2O_8^{2-}]/dt = A[\text{Fe(II)}][N_2H_5^+]/([H^+] + B[N_2H_5^+]) \quad (2)$$

$$\text{rate} = -d[S_2O_8^{2-}]/dt = A[\text{Fe(III)}]/([H^+] + C) \quad (3)$$

(7) Since the rate has inverse hydrogen ion dependence, the three complexes are likely to be $FeS_2O_8{\cdot}N_2H_4^+$, $FeS_2O_8N_2H_4{\cdot}N_2H_5^{2+}$, and $FeS_2O_8{\cdot}(N_2H_4)_2^+$.

The mechanism (4)–(8) may now be suggested.

Hydrolyzed species of iron(III) have not been considered since the hydrolysis constant[24] of $Fe(H_2O)_6^{3+}$ is small. If only $FeS_2O_8{\cdot}N_2H_4^+$ and $FeS_2O_8(N_2H_4)_2^+$ are considered to be

---

[15] S. S. Gupta and Y. K. Gupta, unpublished work.

[16] Ratan Swaroop and Y. K. Gupta, *Indian J. Chem.*, **9**, 361 (1971).

[17] J. D. Miller, *J. Chem. Soc. A*, 2348 (1969).

[18] S. Raman and C. H. Brubaker, Jun., *J. Inorg. Nucl. Chem.*, **31**, 1091 (1969); J. Burgess and R. H. Prince, *J. Chem. Soc. A*, 1772 (1966).

[19] S. S. Gupta and Y. K. Gupta, unpublished work.

[20] F. H. Pollard and G. Nickless, *J. Chromatog.* **4** 196 (1960); W. C. E. Higginson and P. Wright, *J. Chem. Soc.*, 1551 (1955); J. W. Cahn and R. E. Powell, *J. Am. Chem. Soc.*, **76**, 2568 (1954).

[21] H. Sigel, K. Beeker, and D. B. McCormic, *Biochim. Biophys. Acta*, 148, 655 (1967).

[22] H. Sigel, C. Flierl, and R. Greisser, *J. Am. Chem. Soc.*, **91**, 1061 (1969).

[23] E. G. Moorhead and N. Sutin, *Inorg. Chem.*, **5**, 1866 (1966).

[24] D. Seewald and N. Sutin, *Inorg. Chem.*, **2**, 643 (1963).

$$Fe^{3+} + S_2O_8^{2-} \overset{K}{\rightleftharpoons} FeS_2O_8^{+} \tag{4}$$

$$FeS_2O_8^{+} + N_2H_5^{+} \overset{K_1}{\rightleftharpoons} FeS_2O_8\cdot N_2H_4^{+} + H^{+} \tag{5}$$

$$FeS_2O_8\cdot N_2H_4^{+} \xrightarrow{k_1} \text{products}$$

$$FeS_2O_8\cdot N_2H_6^{+} \overset{K_2}{\rightleftharpoons} (FeS_2O_8\cdot N_2H_4\cdot N_2H_5)^{2+} \tag{6}$$

$$(FeS_2O_8\cdot N_2H_4\cdot N_2H_5)^{2+} \overset{K_3}{\rightleftharpoons} (FeS_2O_8(N_2H_4)_2)^{+} + H^{+} \tag{7}$$

$$(FeS_2O_8(N_2H_4)_2)^{+} \xrightarrow{k_2} \text{products}$$

$$Fe^{2+} + S_2O_8^{2-} \xrightarrow{\text{fast}} Fe^{3+} \tag{8}$$

reactive, the decrease in peroxydisulfate is given by (9). All

$$-d[S_2O_8^{2-}]/dt = \{[Fe(III)](k_1K_1[N_2H_5^+]/[H^+] + k_2K_1K_2K_3[N_2H_5^+]^2/[H^+]^2)\}/\{1 + (K_1[N_2H_5^+]/[H^+]) + K_1K_2[N_2H_5^+]^2/[H^+] + K_1K_2K_3[N_2H_5^+]^2/[H^+]^2\} \tag{9}$$

concentrations are equilibrium concentrations except iron(III) which is total analytical concentration. For the range of hydrazine concentration where limiting rate is obtained, the rate law should be independent of hydrazine and that would be possible only when we assume that $FeS_2O_8N_2H_4N_2H_5^{2+}$ and $FeS_2O_8(N_2H_4)_2^+$ are present predominantly and the latter is reactive. Under this condition, (9) reduces to (10) which is

$$-d[S_2O_8^{2-}]/dt = k_2K_3[Fe(III)]/([H^+] + K_3) \tag{10}$$

similar to (3). A plot of $(\text{rate})^{-1}$ vs. $[H^+]$ yields a straight line with positive intercept, and the values of $k_2$ and $K_3$ calculated from the slope and intercept of the line were found to be (4.9 ± 0.5) × $10^{-3}$ $s^{-1}$ and 2.20 × $10^{-3}$ M at 45 °C, (8.1 ± 0.3) × $10^{-3}$ $s^{-1}$ and 2.4 × $10^{-3}$ M at 50 °C, and (14 ± 4.6) × $10^{-3}$ $s^{-1}$ and 2.20 × $10^{-3}$ M at 55 °C, respectively. The energy of activation corresponding to $k_2$ was 21.3 ± 1.3 kcal $mol^{-1}$. $K_3$ is almost independent of temperature, and its average value is (2.25 ± 0.1) × $10^{-3}$ M. The value of $K_2$ was calculated by solving the mass balance equations for Fe(III), $N_2H_5^+$, and the rate data at different [Fe(II)] beyond the maximum in Figure 2. The value of $K_2$ was found to be 176 ± 36 and was almost independent of temperature. Similarly the value of $K_1$ was calculated by solving another set of mass balance equations for the rate data at different Fe(II) and pH before the maximum in Figure 2. The value of $K_1$ was found to be 8.9 ± 2.9 and is independent of temperature in the range studied. There is yet another way of determining the value of $K_1$ from the rate data before the maximum in Figure 2 is attained, by assuming that only $FeS_2O_8^+$ and $FeS_2O_8\cdot N_2H_4^+$ are appreciable and the latter is reactive. The rate law (9) reduces to (11) which is similar to (2). Plots of $(\text{rate})^{-1}$ vs. $[N_2H_5^+]^{-1}$

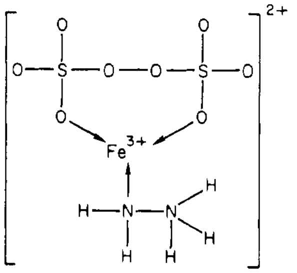
$$-d[S_2O_8^{2-}]/dt = \frac{k_1K_1[N_2H_5^+][Fe(III)]/[H^+]}{1 + (K_1[N_2H_5^+]/[H^+])} \tag{11}$$

at constant $[H^+]$ and of $(\text{rate})^{-1}$ vs. $[H^+]$ at constant $[N_2H_5^+]$ yield straight lines with intercepts as also mentioned earlier. From the slopes and intercepts of these lines, $k_1$ and $K_1$ were calculated and they are given in Table V. The free hydrazine was calculated on the basis of a 1:1 complex of $FeS_2O_8^+$ and $N_2H_4$ and the rate being proportional to the concentration of this complex. The energy of activation for $k_1$ was found to be 7.7 ± 0.2 kcal $mol^{-1}$. $K_1$ is again independent of temperature. It was not feasible to determine $K_1$, $K_2$, and $K_3$ by other methods, owing to the reactivity of the complexes. With these values of different constants, some of the calculated rates have been compared with the observed rates, and agreement between the two is satisfactory.

**Table V.** Values of $k_1$ and $K_1$ from Plots of (11) ($[S_2O_8^{2-}] = 10^{-2}$ M; $I = 0.1$ M)

| $10^3$ × [Fe(II)], M | $10^3$ × $[N_2H_5^+]$, M | $10^3$ × $[H^+]$, M | temp, °C | $10^3k_1$, $s^{-1}$ | $K_1$ |
|---|---|---|---|---|---|
| 0.80 | 0.60–10 | 10.0 | 45 | 2.0 | 10 |
| 1.20 | 0.60–15 | 10.0 | 45 | 2.0 | 11 |
| 5.00 | 4.00–20 | 10.0 | 45 | 2.0 | 6.8 |
| 1.60 | 1.00–20 | 10.0 | 45 | 2.0 | 10 |
| 1.60 | 0.80–20 | 6.76 | 45 | 2.0 | 9.6 |
| 1.60 | 1.00–20 | 3.39 | 45 | 2.0 | 5.9 |
| 1.60 | 2.00 | 1.95–36.3 | 45 | 1.5 | 10 |
| 1.60 | 2.50 | 3.50–35.5 | 45 | 1.5 | 10 |
| 1.60 | 3.00 | 2.35–35.5 | 45 | 1.5 | 9.8 |
| 1.60 | 1.00–19 | 10.0 | 50 | 2.7 | 7.2 |
| 1.60 | 3.00 | 2.35–35.5 | 50 | 2.5 | 10 |
| 1.60 | 1.00–20 | 10.0 | 55 | 3.1 | 7.3 |
| 1.60 | 3.00 | 2.35–35.5 | 55 | 3.2 | 8.4 |

The reaction[20,25] of Fe(III) with hydrazine in aqueous perchloric acid solutions is slow, but in the present case it is not a aquo–iron(III) is complex but a peroxydisulfate complex of iron(III) which might be highly reactive toward hydrazine. A number of instances[26] are known where the aquo–iron(III) complex is less reactive than its chelates with amino polycarboxylic acids, 1,10-phenanthroline, 2,2′-bipyridyl, etc. toward reducing substances which also coordinate with the metal ion and form mixed complexes before undergoing redox reaction. The coordination between Fe(III) and a nitrogen donor molecule in acid medium in general is weak unless it yields a chelate, but a complex with oxygen of sulfur donor molecules can easily take up nitrogen ligands, forming mixed complexes. In the present investigation, Fe(III) may from a chelate with peroxydisulfate through oxygen and then a mixed complex with the following possible structure.



**Registry No.** $N_2H_4$, 302-01-2; $S_2O_8^{2-}$, 15092-81-6; $Fe^{3+}$, 20074-52-6; $FeS_2O_8\cdot N_2H_4^+$, 76757-53-4; $FeS_2O_8\cdot N_2H_4\cdot N_2H_5^{2+}$, 76772-97-9; $FeS_2O_8(N_2H_4)_2^+$, 76772-98-0.

**Supplementary Material Available:** Tables giving the results of stoichiometry, spectrophotometric results of mixtures of iron(III) and peroxydisulfate, and comparison of observed and calculated rates (4 pages). Ordering information is given on any current masthead page.

---

(25) S. S. Gupta and Y. K. Gupta, unpublished work.

(26) G. Nord and O. Wernberg, *J. Chem. Soc., Dalton Trans.*, 845 (1975), 866 (1972); M. M. Taqui Khan and A. E. Martell, *J. Am. Chem. Soc.*, **90**, 3386 (1968); R. Grinstead, *ibid.*, **82**, 3472 (1960); P. V. Subba Rao, B. A. N. Murti, R. V. S. Murty, and K. S. Murty, *J. Indian Chem. Soc.*, **45**, 207 (1978); F. R. Duke and F. R. Parchen, *J. Am. Chem. Soc.*, **77**, 3198 (1955).